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RELATIONS BETWEEN SIMPLE AND COMPLICATED OXYGEN ACIDS[1]

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Introduction

The frequent failure of v-valent chemical elements, Q, to form acids H_vQO_v, or even anions QO_v^{v-}, is an outstanding example of how superficial irregularities in chemical behavior often conceal a grand underlying regularity. Once the simple oxygen acids are inclusively formulated as $H_{v-2n}QO_{v-n}$, it turns out that the simpler and more general behavior is that of $v-n$, and not that of either n or v. Most commonly, the value of $v-n$ encountered is 4, and the only other common values are 3 and 6. The former is typified by the sequence H_4SiO_4, H_3PO_4, H_2SO_4, and $HClO_4$.

The underlying chemical structural basis on which such regularities depend was worked out by Linus Pauling and others some three decades ago. Various $v-n$ values corresponded to various polyhedral arrangements of oxygen atoms around the central "acid-forming" atom Q in the anion QO_{v-n}^{2n-v}. Thus, for a $v-n$ value of 4, we have simple oxyanions that are externally tetrahedra of oxygen. In those exemplified above, 32 electrons are uniformly involved in the outer valence rings of the five component atoms of the anion.

It is important to inquire how far these structural bases and the consideration of quantities similar to $v-n$ can be applied to both simple and complicated oxygen acids, and to the anions and salts they form. First, simple oxygen acids will not be understood completely until their roles in the formation of complicated oxygen acids are understood. Second, the complicated oxygen acids are interesting; collectively, they form a tremendous and significant domain of inorganic chemistry. Finally, certain information common to both simple and complicated oxygen acids can only come from an inclusive delineation of the relations between them.

Nomenclature (Bulloff, 1956)

It is desirable to discuss relations between simple and complicated oxygen salts, and the anions and salts that they form, with a less cumbersome and more defined terminology than that now used. A refinement of suggestions originally made by Sydney Ross leads to the following rules:

1. Oxygen acids, their anions, and their salts shall be called, respectively, oxyacids, oxyanions, and oxysalts. These terms shall refer to species and classes defined below.

2. The simple oxygen acids, containing one atom of an acid forming element,

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Q, formulated as $H_{v-2n}QO_{v-n}$, their anions, QO_{v-n}^{2n-v}, and other ions and salts they form, shall be called, respectively, monoacids, monoanions, and monosalts. Monoanions have been called "monanions" for sake of euphony.

3. The complicated oxygen acids, containing a plurality, p, of atoms of one acid-forming element, Q, all with the same oxidation number, formulated as:

$$H_{p(v-2)+2(1-m)}Q_pO_{p(v-1)+(1-m)},$$

their anions, $Q_pO_{p(v-1)+(1-m)}^{p(2-v)+2(m-1)}$, and other ions and salts that they form, shall be called, respectively, polyacids, polyanions, and polysalts, with the exception that for $p=1$, $n=m$, and Rule 2 applies.

For $p=2$, the particular names are, respectively, diacids, dianions, and disalts.

For $p=7$, the particular names are, respectively, heptaacids, heptaanions, and heptasalts. For euphony, "a" can be undoubled.

For $p=p$, or for $p=\infty$, the particular and/or subgeneric names are, respectively, polyacids, polyanions, and polysalts.

4. The complicated oxygen acids containing a plurality, p, ($p=p_1+p_2+p_3+\ldots+p_h$), of a plurality of different kinds, h, (whether the difference be that of element, of valence or structural configuration state, or other ahylotropic difference) (Bulloff, 1953) of acid-forming atoms, Q (i.e., Q_1, Q_2, Q_3, . . . , Q_h), formulated as:

$$H_{p_1(v_1-2)+p_2(v_2-2)+p_3(v_3-2)+\cdots+p_h(v_h-2)+2(q-1)}(Q_1)_{p_1}(Q_2)_{p_2}(Q_3)_{p_3}\cdots(Q_h)_{p_h}O_{p_1(v_1-1)+p_2(v_2-1)+\cdots+p_h(v_h-1)+(1-q)},$$

their anions,

$$(Q_1)_{p_1}(Q_2)_{p_2}(Q_3)_{p_3}\cdots(Q_h)_{p_h}O_{p_1(v_1-1)+p_2(v_2-1)+p_3(v_3-1)+\cdots+p_h(v_h-1)+(1-q)}^{p_1(2-v_1)+p_2(2-v_2)+p_3(2-v_3)+\cdots+p_h(2-v_h)+2(q-1)},$$

and other ions and salts that can be formed from them, shall be called respectively, heteroacids, heteroanions, and heterosalts.

For $h=1$, Rule 3 applies.

For $h=2$, the particular names are, respectively, diheteroacids, diheteroanions, and diheterosalts.

For $h=3$, the names are, respectively, triheteroacids, triheteroanions, and triheterosalts.

For $h=h$, or for $h=\infty$, the names are respectively polyheteroacids, polyheteroanions, and polyheterosalts.

5. Hetericity, h, is denoted before polyicity, p, in naming.

$H_6Te(MoO_4)_6$ is a diheteroheptaacid.

$H_5I(MoO_4)_3(WO_4)_3$ is a triheteroheptaacid.

$P(W_3O_{10})_4^{---}$ is a diheterotridecaanion.

$(NH_4)_7Ge(VW_2O_{10})(V_2WO_{10})(W_3O_{10})_2$ is a triheterotridecasalt.

6. Neither the hetericity nor the polymericity need be denoted where the name adequately does so.

The diheteroheptacid above is hexamolybdatotelluric acid.

The diheterotridecanion above is tetrakistritungstatophosphate.

7. Where the stoichiometry or structure is not known, or where the known or assumed composition or structure cannot be at present fitted to IUPAC or other accepted nomenclatural system, the name given, while not attempting to innovate a maximal description, shall endeavor to describe all the characterizing features possible that shall not interdict future definitive naming.

   Thus, the triheteroheptacid above may be an accidental 50 mole-percent mixture, or it may be a part-symmetrical ordered displacement. It could be described as a molybdo-tungsto heteroperiodate. Naming the triheterotridecasalt above, were it possible with present limitations of the versatility of IUPAC nomenclature, would probably be less convenient and more confusing than would be the use of the formula instead of a name.

The rules given above, and the special difficulties inherent in the field of this paper, are both observed in the following discussion of the relations between simple and complicated oxygen acids and their derivatives or constituents.

Polyanionization: General

As will be seen in the sequel, aqueous formation of complicated oxyanions, be they heteroanions or any polyanions, follows two general patterns. One is a solvolytic pattern akin to that in the dissociation of simple oxygen acids and in the ionization of simple salts. The second pattern is similar to that occurring in condensation polymerization to form chain, sheet, and net polymers. The possible processes of formation and their aspects can be considered as a single phenomenon of "*polyanionization*."

Three general routes can be postulated for polyanionization. Since the formulae would be similar, it is not necessary to depict separately the more complicated and particular process of *heteroanionization*. These three routes, written in the simplest way, are:

$$pQ_{v-n_1}^{2n_1-v} + 2[p(1-n)+(m-1)]H^+ \rightarrow Q_pO_{p(v-1)+(1-m)}^{p(2-v)+2(m-1)} + [p(1-n_1)+(m-1)]H_2O$$

$$pQ_{v-n}^{2n_2-v} + 2[p(n-1)+(1-m)]OH^- \rightarrow Q_pO_{p(v-1)+(1-m)}^{p(2-v)+2(m-1)} + [p(n_2-1)+(1-m)]H_2O$$

$$p_1QO_{v-n_1}^{2n_1-v} + p_2Q_{v-n_2}^{2n_2-v} \rightarrow Q_pO_{p(v-1)+(1-m)}^{p(2-v)+2(m-1)} \quad (\text{For } p_1+p_2=p;$$

$$m=p_1(n_1-1)+p_2(n_2-1)+1).$$

When the Arrhenius dissociation of water is remembered, it can be recognized that apparent pH restrictions indicated in the particular way of writing these equations chosen are indicative, but not mandatory. Other, and far more complex influences, govern the optimal pH at which a specified polyanionization should be carried out. In general, all three routes can be forced to a desired degree of completion by judicious use of common means for driving a chemical reaction to completion, wherever the desired polyanion can form.

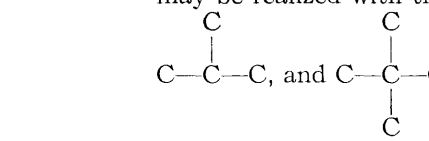
The above equations give no clue as to what polyanions can form. Such clues can come from considering what is already known about the ways in which oxygen polyhedra can be linked with each other.

Polyanionization: Oxygen Tetrahedra

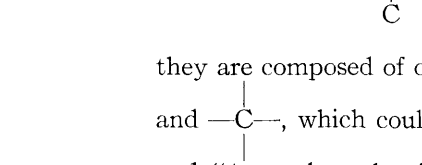
The polyanionization of oxygen tetrahedra, mentioned above for $v-n=4$ for common monanions, offers the classical example of this phenomenon. The classical illustration usually offered considers disilicate, chain silicate, sheet silicate, and network silicate and aluminosilicate formation and symmetry (Eitel, 1954). However, an easier introduction to the subject can be made to tetrahedral linking

by considering the chemistry of carbon, which has long been familiar to most chemists.

In carbon chemistry, tetrahedra may be joined at corners, edges, or faces, as denoted by the familiar notations, respectively, C—C, C=C, and C≡C. A linkage C≡C would imply that two carbon atoms occupy the same space at the same time. Oxygen tetrahedra only join together at corners, two tetrahedrons sharing a single oxygen atom at each corner joined. Thus, the structures that may be realized with them are only those that are analogous to C—C, C—C—C,



C—C—C, and C—C—C, etc. No matter how many of these structures we draw,



they are composed of only four kinds of "structural" units: C—, —C—, —C—, and —C—, which could be termed, respectively, "ends," "middles," "branches," and "4-way branches," respectively involving joinings at 1, 2, 3, and 4 corners of a C-tetrahedron by, respectively, 1, 2, 3, and 4 distinct pairs of electrons. Analogous joinings at 1, 2, 3, and 4 corners of a 4-0-tetrahedron by, respectively 1, 2, 3, and 4 oxygen atoms may be similarly described (Van Wazer, 1958).

In considering the polyanionization of oxygen tetrahedra QO_4^{8-v}, to count each polyanion oxygen only once, corner-shared oxygens shall be considered as contributing $0_{0.5}$ to each oxygen tetrahedron in a polyanion. The valence, v, of the acid-forming element, Q, considered, sets limits upon whether the monanion can go all the way in the successive formation of ends, middles, branches, and 4-way branches, resp., $QO_{3.5}^{v-7}$, QO_3^{v-6}, $QO_{2.5}^{v-5}$, and QO_2^{v-4}. Thus, ClO_4^- can only polyanionize to ends, and can only form Cl_2O_7. SO_4^{2-} can polyanionize to ends to form the dianion $S_2O_7^{2-}$, disulfate, and to middles, which, with two ends, permit the formation of a gamut of polyanions from the trianion, $S_3O_{10}^{2-}$, trisulfate, to the ultimate polyanion $S_pO_{3p+1}^{2-}$, in the limit, SO_3, linear polymeric sulfur trioxide. PO_4^{3-} can polyanionize to ends, middles, and branches; as well as linear, branched and ring polyanions and polymers can form (ibid.). SiO_4^{4-} can give all these forms, and can readily polyanionize to "infinite" sheets and to infinite frameworks or nets of differing spatial "tightness." It can thus be seen that the numerical magnitude of v determines the versimilitude of structures possible for oxygen tetrahedra; similar valence-dependence versatility occurs for other oxygen polyhedra, e.g., pyramids, bipyramids, octahedra, Archimidean antiprisms, etc. However, the primary determinant of relations is the structural symmetry; the valence factor is only secondary. Thus, the other factors, n or m, and p are even more dependent factors. The neglected factor in the study of the relations of simple and complicated oxygen acids and their derivatives is the hetericity, h.

Heteroanionization permits the admission of an element, Q_1, of lower valence, v_1, into the polyanionization of the oxyacid derivatives of an element, Q_2, of a given valence, v_2. The structural unit $QO_{4-0.5x}^{v+x-8}$, where x is the number of corner-

shared O's in the 4−0 tetrahedron can, as has been shown entertain only the x-value permitted by the v-value. Lowering the mean v-value, $\frac{p_1v_1+p_2v_2}{p_1+p_2}$ increases the x-value attainable sometimes. It only takes one oxygen atom join to cross-link two long polyanionized chains together. This fact is of great theoretical and practical importance both for understanding the bulk of terrestrial material and for creating new inorganic compositions. It is already well known in the domain of the silicates (Eitel, 1954), e.g., in the aluminosilicates and in the borosilicates, where the use of tervalent-element tetrahedra permits a multiplicity of network materials to be developed within any given one of the quartzitic structures.

Similarly, heteroanionization has been used to effect terdimensional polyanionization in phosphate-bonded ceramics components (Sheets, 1958). Aluminophosphate "3-way superbranches" were deliberately created to remedy the inability of monheteric phosphoanions to form 4-way branches. In the extreme, the structural unit $AlPO_4$ can crystallize or aggregate in all the ways that the structural unit SiO_2 can, in the solid state, in solution, and in polyphase hydrothermal systems. Polyheteroanionization would probably be even more powerful and versatile in creating inoriganic systems than diheteroanionization.

General Study of Oxyanionic Compounds

The chemistry of some elements is known better than that of others, and for a given element, the chemistry of one of its monanions may be better known than that of another. Similarly, where polyicity is a natural phenomenon, as in the silicates of rocks, minerals, and ores, or where it is of technological interest, as in the phosphates, polyphosphates, polymetaphosphates, and ultraphosphates, interest in the polyanions of some elements exceeds that for other elements. Accordingly, we are still far from a general and complete understanding of monanion and polyanion chemistry.

For heteroanion chemistry, the situation is even less satisfactory. Interest has been small, study has been scanty, definitive findings have been few, and it can be immediately seen that the heteroacids and their derivitives form a vastly larger and more complex field of study than that of all the monoheteric monanions and polyanions put together. It seems likely that as the polyanionization properties of monanions and the heteroanionization properties of monanions and polyanions become better known, that it will be increasingly recognized that before the chemistry of any oxyanion can be understood thoroughly basically, there will have to be a general understanding of oxyanion chemistry for any degree of polyicity and hetericity.

There are already some striking indications of how the study of hetroanions has elucidated the nature of a polyanion in such a way as illuminate the polyanionization of monanions. In figure 1, the heteroanions listed were determined by x-ray crystallography to have the structures formulated. The stoichiometry thus confirmed reflects that of the monanions that provide the central atom of the polyanion. What is surprising is that although WO_4^{2-} and MoO_4^{2-} are electronically and spatially similar, and resemble each other otherwise chemically, in one heteroanion the outer unit coordinated is a trianion, and in the other a monanion. In the polyanion column it can be seen that there is a distinct difference in the polyanions from which the listed heteroanions form. Solution studies have failed to indicate why similar monanions form different polyanions and heteroanions. They have failed to yield structural information. For the polyanions, x-ray diffraction structural information only fell into a meaningful pattern once similar information gave more definitive results for the structure of

the heteroanions. Thus, $Mo_7O_{24}^{6-}$ is isostructural with $Te(MoO_4)_6^{6-}$; it is $Mo(MoO_4)_6^{6-}$, more appropriately a hexamolybdatomolybdate than a heptamolybdate, and it is noteworthy that while the central Mo atoms of the ligand tetracoordinate 4−0 tetrahedra, the central central Mo atom hexacoordinates a 6−0 octahedron from the six ligand tetrahedra. The isostructuralism of $W_{12}O_{40}^{8-}$ and $P(W_3O_{10})_4^{3-}$ is even more startling; the former is $(W_3O_{10})_4^{8-}$ with a hole where the latter has a P^{5+} inserted. While tetracoordination seemingly prevails everywhere, the central 4−0 tetrahedron is formed by oxygens, but the outer W_3O_{10} groups are not linear trianions with a middle joined to the center, but are so arranged that WO_6 octahedra are formed which in turn trace out the 12 corners of a cuboctahedron.

The obvious conclusion is that since isostructuralism can exist for compositions of different hetericity, as in the monanions, steric factors are more primary than hetericity. However, hetericity is a means of establishing the steroechemistry of oxyanions.

Refer again to figure 1; the incredible heterosalt formulated seems at first sight to be tetraheteric. However, it contained originally (Rogers, 1903) 11 V^{V} atoms per V^{III} atom; this would indicate that it is pentaheteric. In solution, one or another of the other atoms present may have accepted some V^{III} electrons, for the $V^{V/III}$ ratio seems to be 13. This may indicate that some forms of the compound are hexaheteric. However, the solution color, and this behavior are compatible with the assumption that the heterosalt is a berthollide (Bulloff, 1953); it is then possible that in principle we might have to understand polyheteroanions in order to explain simpler oxyanions. The relations of simple and complicated oxygen acids to each other are too complex to be more than foreshadowed in this paper.

Particular Study of Heteroanions

In performing experiments intended to show relations between simple and complicated oxyacid derivatives, one must consider the vastness of the field of study marked out by the possible range of polyicity and hetericity if the experiments selected are to be meaningful. Figure 2 shows that the compositional range to be considered leaves out only the noble gases.

As yet, it seems that all chemically active elements can form heterosalts, most of them in a variety of anionic and cationic forms, and many of them in a number of valence states, both usual and unusual. For many candidate structures already known from minerals, or else synthesized in the laboratory, it appears likely that for discrete polyicities alone there will be a multitude of integral-atom compositional variations possible up to a degree of polyhetericity far exceeding any now known.

Thus, the sampling at the potential compound-field of heterosalts, so as to find system among the heteroanions, and among the complicated oxygen acids they could come from or lead to, is a task that could well be lightened. Techniques and approaches that work with small-sized compound fields and simple compounds become either much too slow or too uncertain when applied to large-sized compound fields and to complicated compounds. Indeed, to assure any rate of progress at all, once the simplest ground has been broken, requires the early determination of broad, if not ultimately accurate, working principles, and the location of typical situations and relations for parts of the field of study. Best of all is the early location of a structural rationale that permits the employment of simple structure-unit conceptions and the assumption of an unvarying backbone against which they are to be employed. This is how organic chemistry, the

compound-field of the derivatives of the "carbanes," came into being and progressed as a fruitful field of study. In beginning a study of heterosalts, chemists have yet to range sufficiently far over them. Much would be gained if this preliminary ranging could establish short cuts for further effort. It is the aim of

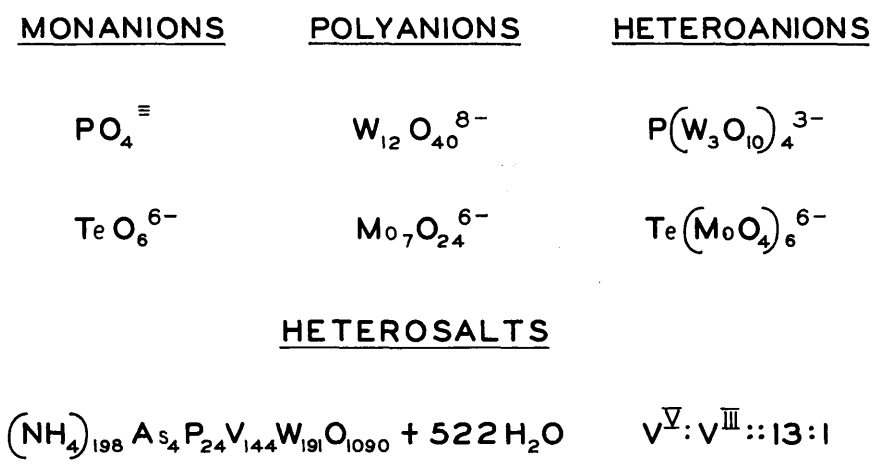


FIGURE 1. Oxyanions

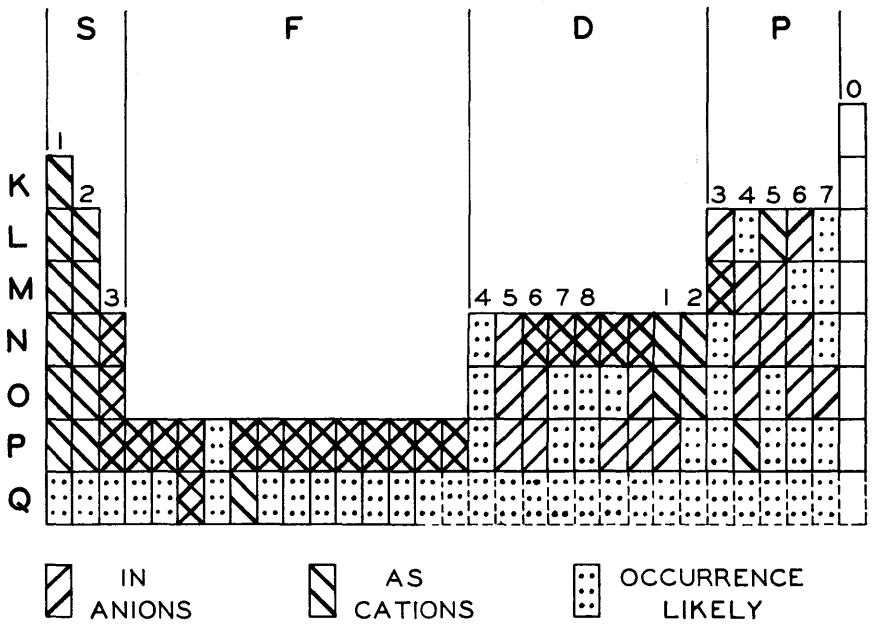


FIGURE 2. Heterosalt constituents.

this paper to show how such short cuts can be uncovered and applied to heteroanion study.

In a complicated and subtle field of study, where slow, definitive techniques such as x-ray crystallography have to be applied with the greatest of care, it might seem brash to consider short cut techniques, particularly those which do not even

involve the use of quantitative analysis. The justification is that these definitive techniques face difficulties when applied to the study of heterosalts that make them either inapplicable or uncertain except for favorable situations or for circumstances that justify the usage of considerable manpower and expense.

Condensation of Anions in Solution

One area in the study of polyanionization that has already consumed considerable effort while only rarely producing unchallengeable results is that of the determination of ionic species in solution. Often polysalts denoted as having a given polyanion in the crystal, and as having an ultimate analysis consonant therewith, have on dissolving either formed another ion, or else the ion has survived definition by a variety of solution-study techniques. Sillén has often spoken of the vast detail that must be attended to before simple complex-ion solutes can be accurately described; the greater difficulties of dealing with more complicated hydrolysis-sensitive ions may explain the low rate of achievement to date in the study of polyanionization in solution.

$$2VO_4^{3-} + 2H^+ \longrightarrow V_2O_7^{4-} + H_2O$$

$$2VO_3^- + 2OH^- \longrightarrow V_2O_7^{4-} + H_2O$$

$$VO_3^- + VO_4^- \longrightarrow V_2O_7^{4-}$$

$$\sim\!\!\sim\!\!\sim\!\!\rightarrow \left[(E_1)_{e_1} (E_2)_{e_2} \text{-------} (E_{E-1})_{e_{E-1}} (E_E)_{e_E} O_X \right]^{\sum_1^E V_E - 2X}$$

$$|E| = \text{HETERICITY} \qquad \left|\sum_1^E e_E\right| = \text{D. P.}$$

FIGURE 3. Condensation.

Figure 3 contrasts the formation of a simple divanadate ion with a simplified formulation of a polyheteropolyanion. The three over-all polyanionization routes for divanadate are shown; vanadium was selected as the example because almost every chemist has been exposed to the classical example of chromate polyanionization, which, since no oxyanion "meta" to the "ortho" chromate exists, has engendered a belief that oxyanion formation is favored only by acidic environment. At the outset, much of the solution study has reflected this orientation in that monanions "ortho" to the probable products that would form have been selected for study, together with a strong acid medium favoring ionization reversal in polybasic acids. Consequently, the number of ionic species present in a single polyanionization has been multiplied unmanageably.

Since heterosalts are often extremely soluble, and frequently highly hydrated, isolating them as formed has often been difficult, and what isolations have been made were not demonstrably those of salts whose anions had been in the solution. Even had this not happened as often as it did, there were reasons why quantitative analysis often failed to give even qualitatively correct results when applied to polyanions and heteroanions.

Limitations of Chemical Analysis

Figure 4 shows two analytical limitations that are common in polyanions; they can be worse for heteroanions. The first is that polysalts or polyacids form numerous hydrates, and, being polybasic, are subject to chemical dehydration as well. Three series of hydration metamers are given, and in each column four species that have been claimed as a definite chemical species in one publication or another are listed. The second is that as more complex stoichiometric ratios are encountered, the analytical precision needed to assign correct formulae becomes less likely to be attained. In a phosphoarsenovanadatomolybdatotungstate, one would expect intercomplexing effects to make the degree of precision of any analysis low.

Figure 5 lists other techniques either difficult to apply quantitatively or to interpret quantitatively when applied to any but fortuitously apt selections of heterosalts. Some of these, however, are useful for short cut work. Two that are particularly useful are light absorption and x-ray powder diffraction. If the solid and solution absorption are quite similar, and if the absorption observed can be tied to the diffraction pattern observed, then the probability that destructive hydrolysis is interfering with the study pursued is somewhat minimized.

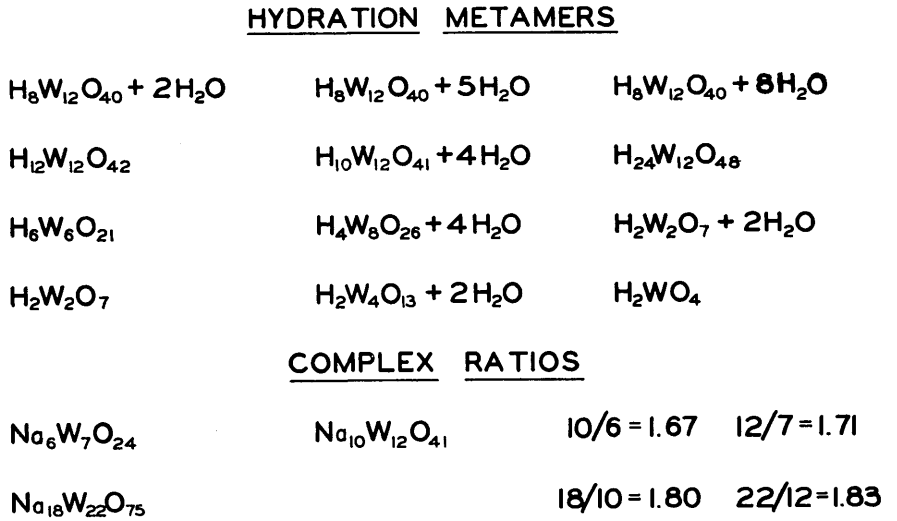


FIGURE 4. Analytical limitations.

Useful Short Cut Procedures for Heterosalt Study

Figure 6 gives some useful short cut procedures for the study of heterosalts. Some of these overlap, but each has its rapid diagnostic uses.

X-ray powder diffraction can be used to "fingerprint" polyanionization products. Line position shifts and line intensities both vary with the size and strain of crystallites, and care has to be taken that improper awareness of these two effects does not lead to the false differentiation of identical heterosalts or to the failure to differentiate between different but similarly structured heterosalts. The role of x-ray powder diffraction will be brought out by the examples of specific study given below.

Spectrophotometry and visual observation of color coupling can both be used in studying the formation of strongly colored polyanions and heteroanions. The

former is better adapted to study of polyanionization products while the latter is most convenient for watching the progress of the polyanionization reaction.

The other short cuts are involved with experimental design rather than with techniques used in experiments, and will be discussed below.

Experimental Test of Utility of Short Cut Procedures

As shown in figure 7, triheteroanions were selected for testing the possibility that laboratory work using short cut procedures could give results that would guide more definitive work or that by themselves would uncover a good deal of knowledge for the effort involved. The results presented cover the equivalent of about one man month of research effort; before triheteroanions were selected

PHYSICAL METHODS	STRUCTURAL METHODS
EQUILIBRIA	POWDER DIFFRACTION
ION PROPERTIES	SINGLE CRYSTAL X-RAY
COLLIGATIVE METHODS	LIGHT ABSORPTION
CRYSTALLOGRAPHY	NUCLEAR RESONANCE
HYLOTROPY	NEUTRON EFFECTS

OTHER TECHNIQUES

FRACTIONATION
SALT FORMATION
DERIVATIVE FORMATION
PARALLEL SYNTHESIS
THERMOGRAVIMETRY

FIGURE 5. Other limitations

POWDER DIFFRACTION	FIELD STUDY
VISUAL ABSORPTION	SUB-FIELD SELECTION
COLOUR COUPLING	COMPONENT STANDARDS

ISOMORPHOUS SERIES

CORROBORATIVE INCIDENTALS

PARTIAL PRODUCTS

FIGURE 6. Short cuts.

and made, however, much more effort was spent making preparations and x-ray powder diffraction photographs of possible precursor monanions, polyanions, and diheteropolyanions so that reactions could be traced, contaminants could be identified, and structural similarities could be detected. Once such preliminary work, which is a part of the facility needed for study has been completed, then it can serve permanently for further work, and each bit of study accomplished eases the path of future studies. It is probable that hundreds of heterosalts can be surveyed per man year in any ordinarily equipped chemical laboratory having access to x-ray and spectrophotometer equipment.

Triheteroanions were selected because proof of chemical individuality and knowledge of chemical structure were lacking for oxyanions more complicated than diheteroanions. To avoid monanions that could possibly polyanionize to networks, or which were prone to give high polymer degrees of polyicity (D.P.), only high-valent elements were selected. To avoid oxidation-reduction complications,

highest-valence state elements that were not vigorous oxidants were employed. This, and other considerations, limited the "field" of the experiment to that shown in figure 7.

If cross-group triheteroanionizations only are considered, the 7 elements of the field yield 7 polyanionization systems, 16 diheteroanionization systems, and 12 triheteroanionization systems. By deferring the study of Nb and Ta, the sub-field shown in figure 7 results; this yields 5 polyanionization systems, 8 diheteroanionization systems, and 4 triheteroanionization systems.

This sub-field was studied in a manner introduced by Allen Rogers (1903) almost six decades ago. Ammoniacal synthesis solutions were used; the OH^- route, which also favored "meta" formation initially, was probably followed initially (Bulloff, 1955). The ammonia was boiled off; as products built up, alkaline degradation and hydrolysis were possibly avoided. As neutrality was reached, perhaps some "ortho" formation resulted, and possibly the "orth"-"meta" combination route was also followed.

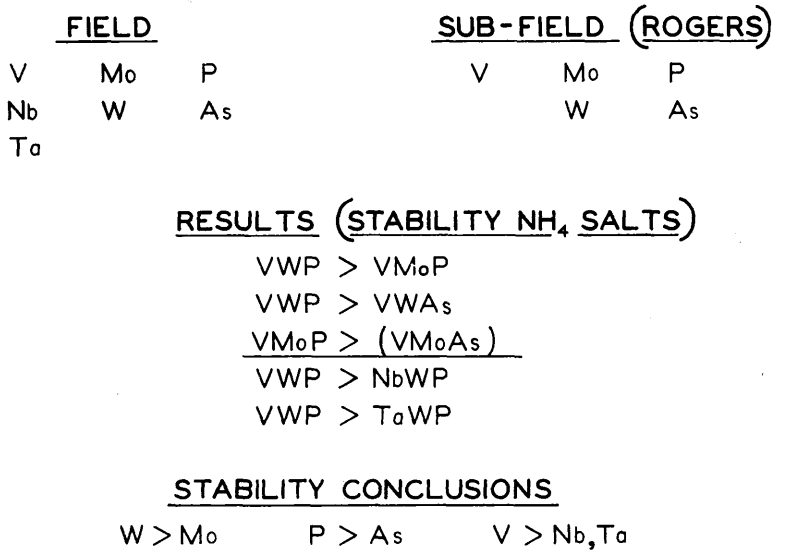


FIGURE 7. Triheteroanion test

The originally colorless-to-yellow solutions turned orange and then red as the boiling of the mixed monanions progressed. The rate of color change was associated with the ease of formation of product. The tungstovanadophosphate was always completely red in 2–3 hr. The yield was extremely high, and a pure product seemed to result. Molybdovanadophosphate solutions were completely red in 3–4 hr; yields were lower, but still high. Tungstovanadoarsenate solutions took 4–5 hr to reach a lighter shade of red; the products were contaminated with about 1% of orange polyvanadate. This impurity was picked out of preparations under a magnifier to secure purer products. Repeated attempts to prepare the molybdovanadoarsenate by this means failed, even after 280 hr of boiling. Yellow molybdoarsenate precipitated during the course of the reaction, and was not altered subsequently.

Since the diheteroanionization products and polyanionization products coulp possibly be contaminants of the triheteroanionization products, the same procedure was employed for these "part" syntheses. In no instance was a red product obtained. Ammonium metavanadate, never observed as a contaminant in triheteroanionization with vanadates was commonly a contaminant in the dihetero-

anionizations, and later, metamonanionates were observed as contaminants in unsuccessful attempts to triheteroanionize niobates and tantalates by Roger's method. These experiments yielded unidentified polyvanadate, molybdovanadate, molybdotungstate, vanadophosphate, molybdophosphate, yellow insoluble molybdoarsenate, tungstophosphate, and tungstoarsenate, as well as the monanions. These, together with purchased ammonium monanionates, polyanionates, and

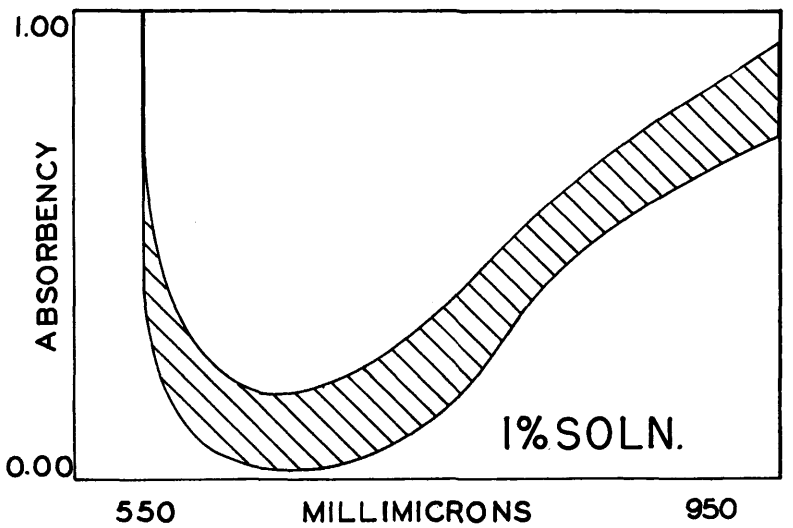


FIGURE 8. Spectrophotometry of crude triheteroanions.

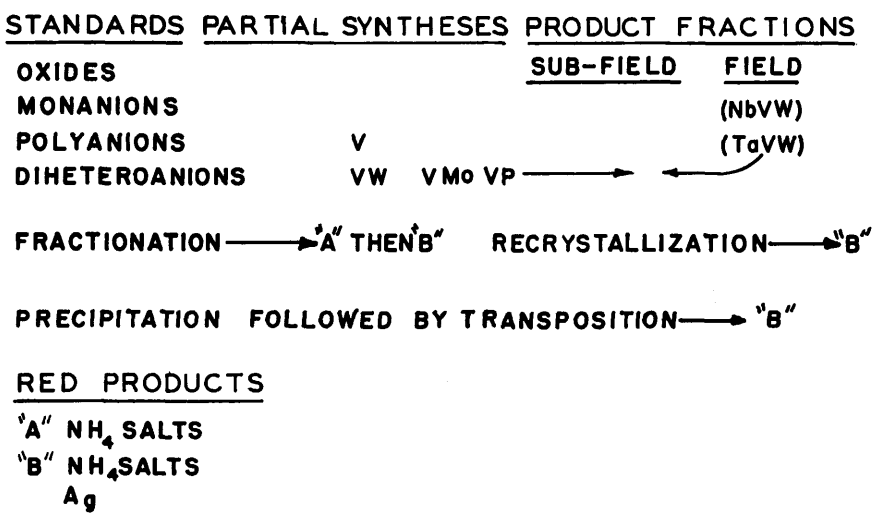


FIGURE 9. X-ray powder diffraction.

diheteroanionates of known composition were subjected to x-ray powder diffraction photography to secure a comparison with the triheteroanion products.

Taking times of formation, and apparent yields and purities as indicators, the stabilities inferred for the ammonium triheteranionates are indicated in figure 7. The attempted triheteroanionization of Nb and Ta gave lightly colored solutions.

One Ta preparation boiled for 580 hr yielded a small crop of black crystals with a triheterosalt diffraction pattern, possibly attributable to V impurity. The conclusion was drawn that under Roger's conditions Nb and Ta triheteroanionates did not form. The bulk of product formed was determined to be precursor tungstophosphate contaminated with, respectively, metaniobate, and metatantalate. Thus, the stability conclusions for individual elements as stated in figure 7 were reached.

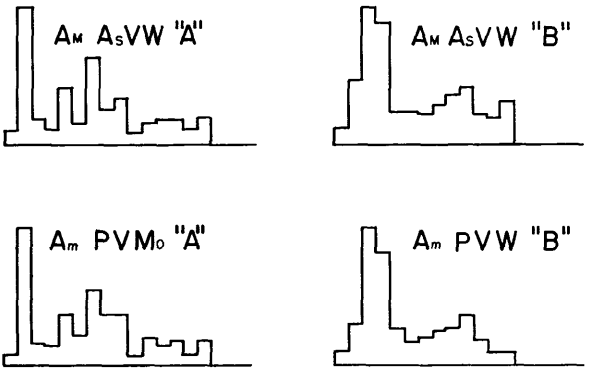


FIGURE 10. Diffraction characteristics.

"A"	"B"	"Ag"	AmVW	AmW
12.6	12.4	9.8	13.2	14
10.91	10.8	8.3	11.0	11
9.76	9.85	5.39	9.7	9.8
7.77	9.27	4.49	7.99	9.3
5.42	8.11	3.38	7.6	8.4
4.85	5.88	3.066	7.26	7.2
4.05	5.42	2.910	7.08	6.39

FIGURE 11. Principal spacings—Å.

A revealing side experiment was performed under Roger's conditions as follows. Normally the full red color of ammonium tungstovanadaphosphate was developed in 2–3 hr. When a maximum of ammonium phosphotungstate was used as the starting material, the red color formed in 0.4–0.6 hr. When vanadium pentoxide was used instead of ammonium metavanadate as the starting material, the 2–3 hr time was reproduced. When vanadotungstate was used no time change was noted, but when vanadophosphate was used, formation time was prolonged. Since the formation of ammonium phosphotungstate in these initially alkaline solutions was not confirmed, it was decided to follow the fate of ammonium phosphotungstate introduced into such solutions in the absence of vanadium. As far as could be determined, it was largely changed to the monanions. Thus the rapid formation noted above, and its implications require further study.

Spectrophotometry of Triheteroanions

As initially crystallized, and then totally dissolved without fractionation, the crude triheteroanion preparations all gave absorption spectra that fell in the shaded range indicated in the graph of figure 8. The refined salts all gave similar parallel spectral absorption curves.

X-Ray Powder Diffraction Patterns of Triheterosalts

The comparison procedure discussed above is schematized in figure 9. It was definitely concluded that trihetroanions had been formed, and that all those formed in a multiplicity of preparations were structurally similar. More convincingly, all of the triheterosalts prepared were dimorphous, and each of the two dimorphous series was an isomorphous series. The data for the "A" and "B" dimorphs are given in figures 10 and 11, along with other data.

In fractional crystallizations of triheterosalts to drop impurities and to establish hylotropy, the first head fraction from the crude synthesis solution was always the "A" dimorph. All subsequent fractions were the "B" dimorph. "A" and "B" mixtures were not observed. It seemed that possibly an impurity organized the nuclei that favored the "A" form; once "A" form was removed from the solution so it could not continue to be a "seed," only "B" form crystals could be obtained. Experiments designed to show that the "A" form was not itself an impurity, but that it was a dimorphic form of the same-structured diheteroanions also demonstrated that the "A" form was monotropically unstable.

Recrystallization of "A" dimorphs gave the "B" dimorphs. Both "A" and "B" gave the same visual absorption spectral curve. Both "A" and "B" forms gave silver trihetroanionates on neutral precipitation with silver nitrate that all had the same x-ray powder diffraction pattern. Transposition of the silver heterosalts with ammonium chloride regenerated only "B" ammonium triheterosalts. Dehydration of "A" and "B" salts showed a possible convergence of x-ray powder diffraction patterns with progressive water loss; however the patterns were increasingly collapsed as dehydration proceeded, and a firm judgment could not be made.

Conclusions of the Short Cut Study

1. Tungstovanadophosphate, tungstovanadoarsenate, and molybdovanadophosphate, but not molybdovanadoarsenate triheteroanions are formed by Roger's boiling together of ammonium monanionates in initially strongly ammoniacal solution.

2. The ammonium triheteroanionates that result are dimorphic, with one of the dimorphs unstable with respect to the other.

3. The rates of formation observed visually and confirmed by yields obtained indicate that vanadium is triheteroanionized under conditions where tantalum and niobium are not, that tungsten triheteroanionized more rapidly than molybdenum, and that phosphorous triheteroanionized more rapidly than arsenic. The yields indicated that the stabilities of the triheterosalts formed may have been in sequence with the formation rates.

4. All the triheterosalt preparations had similar optical absorptions.

5. All the "A" dimorphs were isomorphous and isostructural with each other, and all the "B" dimorphs were isomorphous and isostructural with each other.

6. Both "A" and "B" ammonium heterotrisalts gave the same structured silver heterotrisalts which were transposable to reform only the "B" dimorph.

7. A facility for rapid survey of derivatives of complicated oxygen acids can be easily set up, and once operating, it can be used to classify or survey hundreds of heteropolysalts per man year.

Note

Surveys cannot be extrapolated too far from known structures or compositions. For some oxyanions, x-ray crystal study needed to establish a structure has taken years because the available salt has been of non-optimum symmetry. An immediate short cut contribution would be to seek by survey means a more symmetric less hydrated salt of a given oxyanion whose structure must be known to advance the base for extrapolation study.

Since the above work was done, an effect has been observed which could further be adapted to rapid survey of complicated oxygen acid derivatives. Normally, in x-ray powder diffraction photography of polyheterosalts, care is taken to use x-radiation whose wave length is not near the absorption edge of a constituent element. This is to avoid scatter effects, and "bad" pictures. However, if a "bad" picture is deliberately taken, and compared to a "good" one, it is often possible to establish whether the element with an unfavorable absorption edge has been taken into the product by a synthesis. In some instances, it is even possible to find line effects that hint at spatial relationships. For investigating heteroanions, it is recommended that "good" and "bad" pictures be compared. Thus, for study of tungstomolybdovanadoheteroanionates, it might be instructive to photograph each comparison specimen with copper, chromium, technitium, and rhenium x-rays.

SUMMARY

Relations between simple and complicated oxygen acids can only be completely understood in terms of a general knowledge of oxyanions. This same general knowledge is needed in order to complete our knowledge of simple oxygen acids.

The study of complicated acids and their derivatives can be expedited by short cut techniques adapted to survey procedures in order to make maximal use of the minimal amount of definitive structural information that can be made available in a limited time.

A tentative terminology has been suggested for complicated oxygen acids and their derivatives which has some advantages over present terminology.

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